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# PHOTOELECTROCHEMICAL PHENOMENA ON SEMICONDUCTOR REDOX GLASS ELECTRODES

**ELISABETA VERESS[a], VICTOR LITEANU[a], IULIU O. MARIAN[b], ANDREEA OLTEAN[b]**

*"Babeş-Bolyai" University, Faculty of Chemistry and Chemical Engineering*
*[a] Department of Inorganic Chemistry, [b] Department of Physical Chemistry,*
*11 Arany Janos Street, RO-3400 Cluj-Napoca.*
*E-mail: iomar@chem.ubbcluj.ro*

**ABSTRACT.** Photoelectrochemical properties of the $SiO_2$-$Na_2O$-$B_2O_3$-$Fe_2O_3$-FeO-$Al_2O_3$ semiconductor glass are investigated in order to evaluate the radiation contribution to the electrode potential of redox sensors. For this purpose the open circuit phototension was determined in the presence of the $Fe(CN)^{3-}_6$ / $Fe(CN)_6^{4-}$ redox couple, depending on the incident radiation power and the working electrolyte pH, using 514.5 and 488.0 nm laser excitation. The nearly logarithmic shape of the $\Delta U_{ph}^{oc}$-P function in visible domain (514.5 and 488.0 nm) corresponds to an Schottky junction.

## Introduction

Partial substitution of $SiO_2$-$Na_2O$ or $SiO_2$-$Li_2O$ glasses by transition metal oxide that can exist in different redox state in glass results in the appearance of electronic conduction too. The predominance of one of the other conduction type depends on the nature and content of the substituent [1,2]. In the case of predominantly electronic conductor glasses transport mechanism is considered to be an activated electron transfer between the transition metal ions in different oxidative states. These glasses behave as n-type semi-conductors [2,5].

Semiconductors glass membranes exhibit redox sensitivity (redox potentiometric electrode function) if both the free electron activation energy ($E_a$) and the membrane electrical resistivity ($\rho$) are sufficiently low, namely, $E_a$ = 0,3 eV and $\rho < 10^6$ ohmcm [2,4].

The following study evaluates the radiating contribution to the electrode response of $SiO_2$-$Na_2O$-$B_2O_3$-$Fe_2O_3$-FeO-$Al_2O_3$ glass electrodes used as potentiometric redox sensors.

Therefore, the photo response (phototension $\Delta U_{ph}^{oc}$ *vs* incident radiation power (P) of irradiated electrodes was determined in the presence of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couple, at different pH values of the support solution.

**Experimental**

Photoelectrochemical determinations were carried out using an electrochemical cell containing the redox glass working electrode and a Pt ring counter electrode.

Redox glass electrodes were constructed as follows: The 1,5-2mm thick semiconductor membranes were made from a $SiO_2$-$Na_2O$-$B_2O_3$-$Fe_2O_3$-FeO-$Al_2O_3$ glass containing 8mol % of $Fe_2O_3$ and FeO. On the internal side of the membrane ohmic contact was assured through an Hg bridge. The external membrane surface's zonal control requirements were assured by polishing with 0,3µ $Al_2O_3$ powder.

Working electrolytes were freshly mixed from 0.1 M $K_3$ [Fe $(CN)_6$] and 0,1 M $K_4$[ $Fe(CN)_6$] stock solution prepared in pH buffers of pH = 4.01 (0.05M KH phtalate); 6,86 (0,025M $KH_2PO_4$ + 0,025M $Na_2HPO_4$) and 9,18 (0,05M borax). Concentration ratios of oxidized and reduced species were fixed at [ox]:[red] = 1:100 ($c_1$) and 100:1 ($c_2$), respectively.

Determinations were made on normal light incidence. As light sources, Ar ion laser (488.0 and 514.5 nm) was utilized. Incident laser beam power (P) was varied between 20 and 120 mW for both wavelengths. The incident light power was measured with an LM-2 (Karl Zeiss) type power-meter.

Photo response ($\Delta U_{ph}^{oc}$) measurements were performed in open circuit conditions using fresh working solutions. The dark potential value ($U_d$) was measured at all times.

The pH response of the semiconductor glass electrode was determined between pH=1 and 12, in glycine - HCl and glycine - NaOH buffer solutions, respectively [prepared from 0.1 M glycine + 0.1M NaCl; 0.1M HCl and 0.1 NaOH stock solutions].

Electronic measurements were carried out with usual laboratory purpose digital pH meter (± 1 mV sensitivity).

All solutions were prepared from analytical grade reagents, in demineralised water.

**Results and discussion**

On basis of the experimental data corresponding to 514.5 and 488.0 nm (as seen below) it may be presumed that at relatively larger power values the $\Delta U_{ph}^{oc}$-P function would become logarithmic.

Photo responses obtained at 514.5 and 488.0 nm approach the open circuit values ($\Delta U_{ph}^{oc}$) expected for an Schottky junction [6].

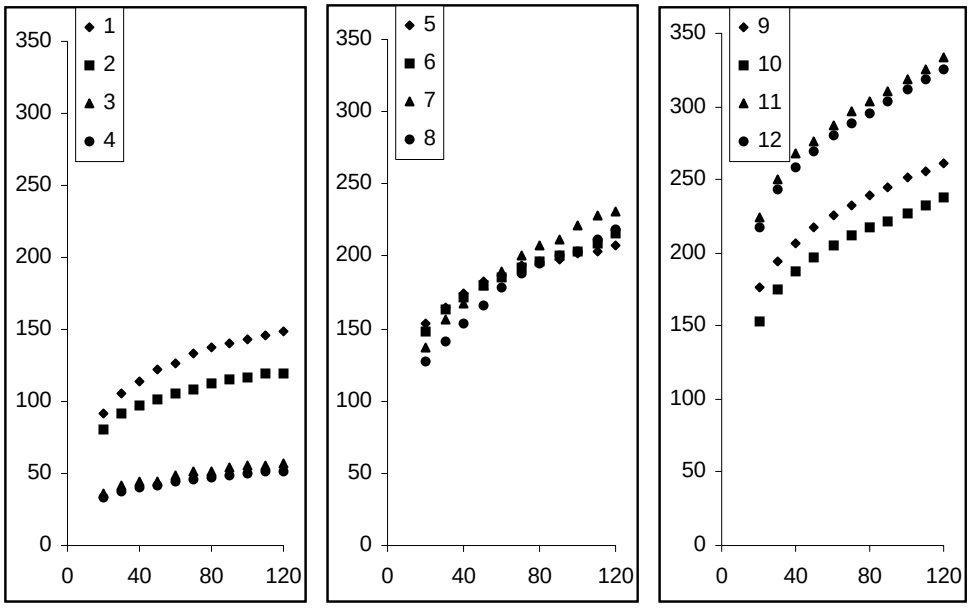


**Fig. 1.** Photo response $\Delta U_{ph}^{oc}$ (mV) *vs* P (mW) obtained at pH = 4 (a); pH = 6.9 (b); pH = 9.2 (c), using Ar ion laser excitation: $c_1$ solution at 488 nm (♦); $c_1$ solution at 514,5 nm (■); $c_2$ solution at 488 nm (▲ ); $c_2$ solution at 514.5 nm (●)

$$\Delta U_{ph}^{oc} = \beta_s kTe_0^{-1} \ln (j_L j_S^{-1} + 1) \quad (1)$$

The value of empirical coefficient $\beta_S$ is determined by experimental conditions; current density $j_L$ is proportional to the incident radiation power and $j_S$ is the saturation current density, respectively.

The $\Delta U_{ph}^{oc}$-P curves presented on Fig.1 have logarithmic shapes. In this powers range, experimental data fit fairly well the empirical expression:

$$\Delta U_{ph}^{oc} = K \ln (P + 1) \quad (2)$$

in accordance with eq. ( 1 ),considering that P = *const*·$j_L$ and K = $t_S \cdot kTe_0^{-1}$

At power values larger than 100mW the shape of the $\Delta U_{ph}^{oc}$–P curves is slightly changed, probably due to the interfering nonradiative effects occurring in the depletion region of the semiconductor surface.

The influence of the working solution's pH is considerable. The extent of the pH effect differs for solution $c_1$ and $c_2$. Because of this, the succession of the nearly parallel curves $c_1$ and $c_2$ corresponding to the same wavelength on Fig. 1c (pH = 9.2) is inversed vs. that on Fig. 1a (pH = 4). At pH = 6.9, the very close curves intersect at about 50 mW (488.0 nm), and at about 95 mW (514.5nm), respectively (Fig.1b). From the table 1 the values of correlation coefficients r [7] are close to unit and represent a good choice of log-fits [7].

The relatively reduced differences observed between K values corresponding to the same solution at different wavelength of the incident radiation may be associated with the nonradiative effect. The pH influence acts through the modification of the empirical $\beta_S$ coefficient and produces larger differences (see Table 1).

**Table 1.**

Values of K fitted from experimental data

| Trial | Slope K / mV | Noise* / mV | ∠r∠ | $100 \cdot r^2$ / % |
|---|---|---|---|---|
| 1 | 30.93167 | 1.18 | 0.9979 | 99.57 |
| 2 | 25.62451 | 1.92 | 0.9881 | 97.63 |
| 3 | 11.86609 | 0.58 | 0.9963 | 97.27 |
| 4 | 10.78779 | 0.27 | 0.9990 | 99.80 |
| 5 | 45.08126 | 8.10 | 0.8830 | 77.97 |
| 6 | 45.26659 | 4.95 | 0.9709 | 94.26 |
| 7 | 46.98645 | 4.96 | 0.9869 | 97.40 |
| 8 | 43.69968 | 6.13 | 0.9789 | 95.82 |
| 9 | 54.93272 | 4.08 | 0.9883 | 97.68 |
| 10 | 49.72481 | 2.13 | 0.9967 | 99.33 |
| 11 | 69.94974 | 6.10 | 0.9833 | 96.68 |
| 12 | 68.22529 | 4.98 | 0.9890 | 97.80 |

** standard deviation of adequacy*

The constancy of the potential values without laser excitation indicates that the effect of directly induced thermal modifications due to the nonradiative recombination effects with the bulk solution was negligible.

Redox potential values obtained with platinum measuring electrode in the working aqueous solutions agree with formerly published data [8]. The variation of the phototension with pH indicates that the effect observed on glass redox electrodes has other origin, correlated with the stability of electrodic surface.

In search of explanations, the U = f (pH) function has been determined for the studied glass electrodes in the range of 1 ÷ 12 pH (see Fig. 2). It shows a quite close resemblance with the pH dependence of the flatband potential of certain oxidic semiconductors [9], presenting a similar irregularity about pH = 7.

In case of oxidic semiconductors the flatband potential $U_{fb}$ varies with the pH of solution in accordance with the Gerischer equation [9]:

$$-\partial U_{fb}/\partial pH = 2{,}3\ kTe_0^{-1}/[1+(kTe_0^{-1})(C_H e_0^{-1})(N_{MeOH}^{+}+N_{OMeOH}^{-})^{-1}] \quad (3)$$

$C_H$ is the Helmholtz capacitance and $N_{MeOH}^{+}$, $N_{OMeOH}^{-}$ are the concentrations of charged species on oxidic semiconductor surfaces according to the following adsorption equilibria:

$$OMe + H_2O \Leftrightarrow OMeOH^- + H_3O^+ \quad (4)$$

$$MeO + H_3O^+ \Leftrightarrow MeOH^+ + H_2O \quad (5)$$

MeO and OMe being the disposable (active) surface adsorption centres.

Therefore, the $U_{f,b}$ – pH dependence is determined by the changes produced in the chemical activity (a) of the charged species adsorbed on the semiconductor surface.

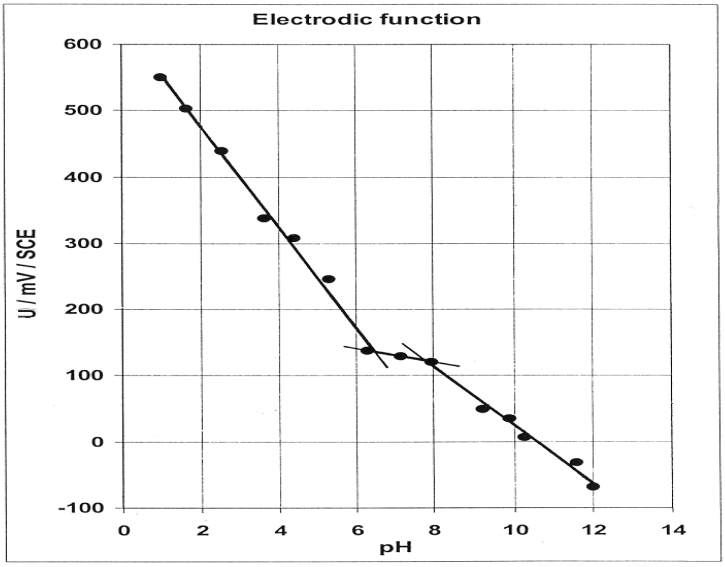


**Fig. 2.** The pH response of the semiconductor glass studied

It may be considered that similarly, in the case of semiconductor oxidic glasses, the modification of the potential is determined by the surface – adsorbed charged species ($H_3O^+$ and $OH^-$) concentration, which similarly, beside the pH, depends on the global composition of the working solution and the discreteness of charge effect. The electrodic function present three domain in pH units (1;6.54), (6.54;7.78) and (7.78;12). In alkaline domain because of considerable change of chemical activity with of amount of surface charge (see second term of denominator in eq. 3) the slope of potential *vs* pH is 43.89 mV/pH, and a good functional dependence (R=0.992). The great values 75.37 mV/pH in the acidic range (R=0.996) indicate another aspect related by the "discreteness of charge effect". This can explain too, why the pH due modifications of the potential becomes significant only if the concentrations of coexisting oxidized and reduced species in the solution differ significantly

and in same time why the electrostatic term in electrochemical potential of the adsorbed ions is the local potential at the place of the ion and not the potential at the surface of oxidic semiconductor.

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